

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ³ : B32B 31/28; G03C 5/00	A1	(11) International Publication Number: WO 83/ 02254 (43) International Publication Date: 7 July 1983 (07.07.83)
<p>(21) International Application Number: PCT/US82/01767</p> <p>(22) International Filing Date: 20 December 1982 (20.12.82)</p> <p>(31) Priority Application Number: 336,339</p> <p>(32) Priority Date: 31 December 1981 (31.12.81)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: WESTERN ELECTRIC COMPANY, INC. [US/US]; 222 Broadway, New York, NY 10038 (US).</p> <p>(72) Inventor: BOSCH, Martin, Albert ; 9 Braeburn Drive, Lincroft, NJ 07738 (US).</p> <p>(74) Agents: HIRSCH, A., E., Jr. et al.; Post Office Box 901, Princeton, NJ 08540 (US).</p> <p>(81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent).</p>		<p>Published <i>With international search report.</i></p>
<p>(54) Title: OPTICAL RECORDING MEDIA</p> <div data-bbox="430 1224 1258 1656" data-label="Image"> </div> <p>(57) Abstract</p> <p>An optical storage medium for the storage of information is produced by employing a material (4) having a solid matrix upon irradiation with a suitable form of energy undergoes a generation or increase of gas pressure within a solid matrix. To write information in the medium, energy is directed to a localized area. The energy, if appropriately chosen, produces a desired gas pressure which deforms the surface (8) of the medium in the localized area. Indeed, if sufficient energy is applied, the gas pressure is sufficient to remove (11) the material in the localized area. Either the removal of material or the production of a surface irregularity produces an optically observable change relative to the unexposed regions of the medium. In this manner, it is possible to store information in the medium. Upon reading, using standard techniques, a high signal to noise ratio signal is obtainable.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	LI	Liechtenstein
AU	Australia	LK	Sri Lanka
BE	Belgium	LU	Luxembourg
BR	Brazil	MC	Monaco
CF	Central African Republic	MG	Madagascar
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SE	Sweden
FR	France	SN	Senegal
GA	Gabon	SU	Soviet Union
GB	United Kingdom	TD	Chad
HU	Hungary	TG	Togo
JP	Japan	US	United States of America
KP	Democratic People's Republic of Korea		

- 1 -

OPTICAL RECORDING MEDIA

Background of the Invention1. Field of the Invention

5 This invention relates to optical storage media.

2. Art Background

A variety of optical storage schemes have been proposed. Although these schemes vary widely in specific detail, they all have a certain aspect in common -- the optical storage medium undergoes a modification which is observable as an optical change upon irradiation with energy such as light. For example, an optical recording medium has been proposed that utilizes an emulsion of dispersed silver. The silver absorbs the incident energy being employed for writing. After sufficient energy is absorbed, the heat generated by absorption melts the material in a localized area. In this manner, a void is formed which provides a detectable optical change in the medium. A problem with this system, however, is that the signal to noise ratio upon reading of the stored information is relatively low.

Summary of the Invention

An optical storage medium includes trapped gas atoms or molecules or a source of gas which gas undergoes an expansion of volume when the medium is exposed to an information writing source of energy. The gas expansion causes localized deformations of the storage medium, which deformations serve to store the written information.

Description of the Drawings

30 FIG. 1-3 show examples of the types of distortion produced in optical recording media according to the invention.

Detailed Description

The recording media in accordance with this invention include a material having (1) a solid network,



- 2 -

i.e., a network of bound atoms as the supporting structure, and (2) atoms or molecules of a gas or gas precursor which are bound to or trapped in the network. The material is further chosen so that application of energy in a localized area of the medium produces internal pressure in this area through the generation of a gas from the gas precursor and thus increase in gas pressure, or through the increase in the vapor pressure of a trapped gas. The material is further chosen so that the gas is generated or the vapor pressure is increased while maintaining the solid network. In this regard some insubstantial amount of melting is tolerable. However, the regions of the medium where the gas is generated or the gas pressure is increased should remain essentially totally solid. The increased internal pressure induces a deformation in the solid network and results in a concomitant deformation in the medium surface. In the extreme, when the pressure has increased sufficiently (generally quite substantially) voids are formed. Either the surface deformation or the voids provide an observable optical change which is readable with a relatively high signal to noise ratio.

For example, materials such as hydrogenated amorphous silicon, i.e., silicon having a bound hydrogen content in the range 4 atomic % to 50 atomic %, hydrogenated amorphous germanium, i.e., germanium having a bound hydrogen content in the range 4 atomic % to 50 atomic %, hydrogenated indium arsenide (4 to 40 atomic % hydrogen), and other hydrogenated materials, e.g., tin, tin oxide and tellurium, are suitable as a recording medium. As shown in FIGS. 1-3, the optical medium can be in the form of a layer 4 supported on a substrate 6 of, for example, glass. In any of these embodiments, the application and absorption of energy, e.g., electromagnetic energy from a laser, such as the 5145 Å line from an argon ion laser, causes the evolution of hydrogen gas. As the gas, e.g., hydrogen, is evolved, the chemical binding structure of the material is modified but the material



- 3 -

remains in the solid phase. Since the solid phase is maintained, pressure builds in the recording medium. This pressure is relieved through the deformation, 8 in FIG. 1, of the surface of the medium. The greater the hydrogen evolution the greater the degree of deformation. Indeed, for materials, such as hydrogenated germanium, after deformation some material is rearranged by the increasing pressure to form pores, 10 in FIG. 2. With even greater energies, the resulting pressure from the evolved hydrogen produces the total removal of solid material in a localized area as shown at 11 in FIG. 3, by, in essence, an explosive process. After the application of energy, the solid network generally becomes more stable in the areas where writing energy has been applied. Using a laser beam, information bits can be written onto the medium at a spacing generally equal to the size of the deformations produced in the writing process.

The energy employed to evolve a gas and/or increase the pressure of an existing gas depends on the absorption of energy by the medium being utilized. For the aforementioned materials, for example, electromagnetic radiation in the wavelength range from $0.3 \mu\text{m}$ to $1.0 \mu\text{m}$ is used. Other forms of radiation such as electron beams can be used. It is generally preferred to deposit a thin layer of the recording medium on a supporting substrate. Thicker, self-supporting medium layers can be used, but the thicker the medium layer, the greater the material and processing costs.

Additionally, the writing energy necessary to bring the gas pressure to a level sufficient to achieve a deformation in the medium surface increases, up to a point, with medium thickness. Suitable materials preferably have a relatively large absorption coefficient for electromagnetic radiation. Thus, incident energy is absorbed typically within 5000 \AA of the surface. In this



- 4 -

manner, the gas evolved or the gas pressure is increased also within this distance. It follows that, for light writing sources, additional thickness of the medium beyond about 5000 Å generally does not substantially affect the energy required or the extent of gas pressure generated, but does increase cost. (For energy such as high-energy electrons, penetration is much deeper and thus deeper regions in the medium are also affected.) Additionally, the thicker the medium, the greater is the gas pressure, and thus the greater the absorbed energy, necessary to produce the desired deformation, i.e., a deformation producing a perceivable optical change, preferably a reflectivity change of at least 20 percent. To maintain nominal writing energies, media thicknesses in the range 0.01 Mm to 1.0 Mm are typically employed. For exemplary materials such as hydrogenated amorphous silicon, hydrogenated amorphous germanium and hydrogenated amorphous indium arsenide, energies in the range 5.0 to 15 nJoules/ μm^2 , 2.5 to 7 nJoules/ μm^2 , and 1.0 to 5 nJoules/ μm^2 , respectively, are advantageously utilized with medium thicknesses in the range 0.01 μm to 1.0 μm .

For preferred writing speeds, e.g., 5 to 10 Mbits per second, power densities in the range 10 mW to 150 mW supplied to the area to be written are used.

Suitable media for the practice of the invention are produced by conventional techniques such as reactive sputtering. For example, in the case of hydrogenated amorphous silicon or hydrogenated amorphous germanium, a silicon or germanium target, respectively, is bombarded with ions such as argon ions. This bombardment and subsequent reaction with hydrogen is accomplished by striking a plasma in an atmosphere containing an inert gas such as argon together with hydrogen. Argon to H_2 mole ratios in the range 3:1 to 2:1 are advantageously employed at a total pressure from 2 to 30 mTorr. In these environments r.f. power densities of 0.1 to 2 watts/ cm^2 are sufficient to produce a plasma. A suitable deposition



- 5 -

substrate such as a glass substrate is placed in the plasma with the surface on which the deposition is to occur facing the target. The substrate is maintained at a temperature of 250 degrees C for silicon and 100 degrees C for germanium. (Lower temperatures result in decreased hydrogen content in the deposited material.) The sputtered material, e.g., silicon or germanium, reacts with the hydrogen and deposits on the substrate. The partial pressure of the hydrogen present during reactive sputtering determines the amount of hydrogen incorporated into the amorphous material.

Similarly to produce hydrogenated amorphous indium arsenide, indium arsenide is deposited on a substrate by conventional techniques such as molecular beam epitaxy. For example, a resistively heated oven containing indium and one containing arsenic are used as sources of these materials. The temperatures of the ovens determine the indium and arsenic content of the indium arsenide in the film. (Films that are slightly arsenic rich exhibit somewhat lower energy requirements for writing.) A substrate is placed in the vapor flow from these boats and indium arsenide is deposited. The deposited indium arsenide is then placed in a hydrogen atmosphere and a plasma is struck in the gas (50 mTorr to 200 mTorr pressure) with, for example, an r.f. power density in the range 0.01 to 0.5 watts/cm². Other techniques such as glow discharge decomposition of silanes, pyrolytic decomposition of materials such as silanes and germanes, homogeneous chemical vapor deposition of, for instance, silanes and germanes are also suitable for producing solid medium which upon application of energy experiences an increased internal gas pressure.

Similar processes can be used to produce media of other materials. For example, for tin and tin oxide, the target to be sputtered is of tin, the plasma atmosphere is at 20mTorr, and the ratios of the plasma constituents are: 20(argon): 1(hydrogen) for the hydrogenated tin medium, and



- 6 -

100(argon): 5(hydrogen): 1(oxygen) for the hydrogenated tin oxide medium. For a tellurium medium, the target is of tellurium, and the plasma ratio is 100(argon): 10-20(hydrogen).

5 The foregoing data is by way of example only. Other processing techniques and device parameters can be used.

Typically, a hydrogen concentration of the amorphous silicon or germanium material in the
10 range 4 atomic % to 50 atomic % and 4 to 40 atomic % in amorphous indium arsenide is desirable. A hydrogen content of less than 4 atomic % typically produces unacceptably irregular deformations in the surface of the recording
15 medium upon writing, e.g., deformations typically at least two times the writing spot size that are generally formed from a plurality of smaller irregular shaped deformations. Such irregular deformations lead to relatively low optical changes. Higher hydrogen content generally lead to lack of long-term stability for the films.

20 Reading of the stored information is done using known techniques relying upon the optical characteristic changes produced in the medium by the writing process.



- 7 -

Claims

1. A process for storing information in a storage medium comprising the steps of applying energy to a localized area of said storage medium and through the application of said energy producing a change in said localized area which is perceivable as an optical change

CHARACTERIZED IN THAT

- said storage medium comprises a solid body (4) which upon application of said energy experiences an increased internal gas pressure that produces a modification (8, 10, 11) of the surface of said medium.

2. The process of claim 1 wherein said internal gas pressure results from the generation of hydrogen.

3. The process of claim 2 wherein said storage medium comprises hydrogenated amorphous silicon.

4. The process of claim 2 wherein said storage medium comprises hydrogenated amorphous germanium.

5. The process of claim 2 wherein said storage medium comprises hydrogenated amorphous indium arsenide.

6. The process of either claim 2, 3, or 4, wherein storage medium comprises a hydrogen atomic percent in the range of 4 to 50.

7. The process of claim 2 wherein said storage medium comprises hydrogenated tin.

8. The process of claim 2 wherein said storage medium comprises hydrogenated tin oxide.

9. The process of claim 2 wherein said storage medium comprises hydrogenated tellurium.

10. The process of claim 1 wherein said modification comprises a void.

11. The process of claim 1 wherein said modification comprises a rise in said surface.

12. A product formed by the process of storing information in a storage medium comprising the steps of applying energy to a localized area of said storage medium and through the application of said energy producing a change in said localized area which is perceivable as an



- 8 -

optical change

CHARACTERIZED IN THAT

said storage medium comprises a solid body (4) which upon application of said energy experiences an increased internal gas pressure that produces a modification (8, 10, 11) of the surface of said medium.

13. The product of claim 12 wherein said internal gas pressure results from the generation of hydrogen.

14. The product of claim 13 wherein said storage medium comprises hydrogenated amorphous silicon.

15. The product of claim 13 wherein said storage medium comprises hydrogenated amorphous germanium.

16. The product of claim 13 wherein said storage medium comprises hydrogenated amorphous indium arsenide.

17. The product of claim 13, 14 or 15 wherein storage medium comprises a hydrogen atomic percent in the range 4 to 50.

18. The product of claim 13 wherein said storage medium comprises hydrogenated tin.

19. The product of claim 13 wherein said storage medium comprises hydrogenated tin oxide.

20. The product of claim 13 wherein said storage medium comprises hydrogenated tellurium.

21. The product of claim 12 wherein said modification comprises a void.

22. The product of claim 12 wherein said modification comprises a rise in said surface.



I/I

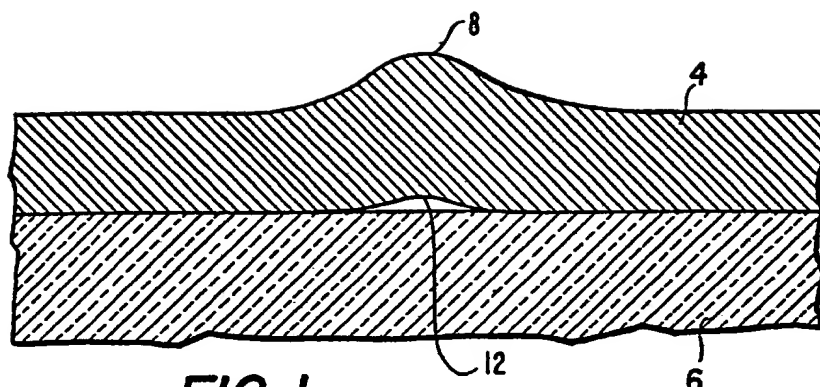


FIG. 1

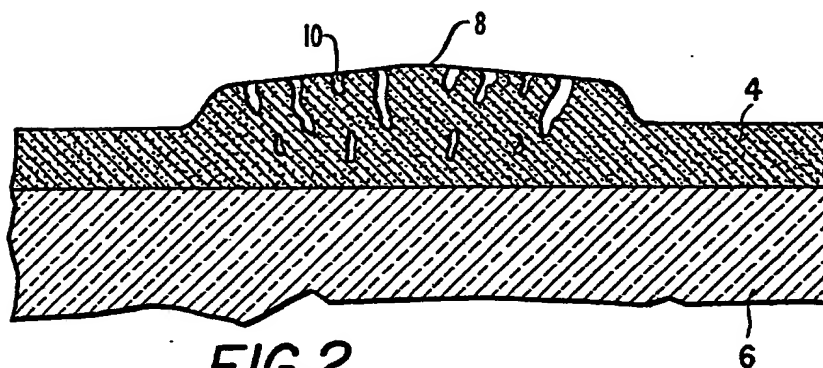


FIG. 2

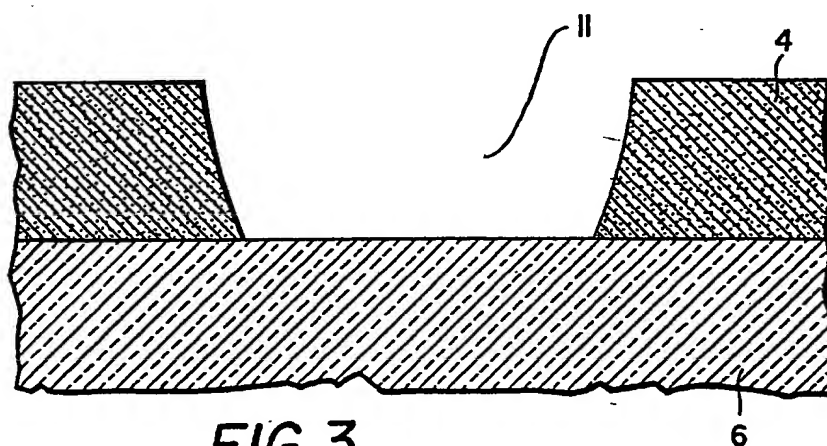


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US82/01767

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ³ B32B 31/28; G03C5/00		
U.S. CL. 430/290		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	204/291, 292; 313/391, 392; 346/1.1, 76L, 76R, 77R, 135.1; 427/74.93; 430/11, 17, 50, 84, 85, 290, 320, 321, 495, 945	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁸ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X, P	US, A, 4,357,179, (Adams et al.) 02 November 1982	1, 4, 6, 10-15, 17, 21-22
X	US, A, 4,255,686, (Maruyama et al.) 10 March 1981	1-3, 6, 10-14, 17, 21-22
X	US, A, 4,217,374, (Ovshinsky et al.) 12 August 1980	1-22
X	US, A, 4,265,991, (Hirai et al.) 05 May 1981	1, 3, 5, 6, 10-14, 16, 17, 21-22
X	US, A, 4,289,822, (Shimada et al.) 15 September 1981	1-6, 10-17, 21-22
X	US, A, 4,147,667, (Chevallier et al.) 03 April 1979	1-4, 6, 7, 10-15, 17-18, 21-22
X, P	US, A, 4,357,616, (Terao et al.) 02 November 1982	1-22
X, P	US, A, 4,340,662, (Ovshinsky et al.) 20 July 1982	1, 2, 6, 9-13, 17, 20-22
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
31 March 1983	12 APR 1983	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	<i>Charles Z. Bowen Jr.</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	US, A, 4,265,720 (Winstel) 05 May 1981	1-3, 6, 10-14, 17, 21-22
A	US, A, 4,307,408 (Kiyohara et al.) 22 December 1981	1-22
A	US, A, 4,278,734 (Ohta et al.) 14 July 1981	1, 2, 6, 8, 10-13, 17, 19, 21-22